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CHEMICAL REACTIONS UNDER ULTRA HIGH PRESSURE. UREA SYNTHESIS FROM SOLID AMMONIUM CARBONATE.

By RYO KIYAMA and TAKAO YANAGIMOTO.

Introduction.

It is well-known¹⁾ that urea may be synthesized by the dehydration of ammonium carbonate at high temperature and high pressure, but it has scarcely been studied because of less yield of urea is expected as compared with the method of direct synthesis from ammonia and carbon dioxide.

As an example of the chemical reactions under high pressure, the effect of hydrostatic pressure on the urea synthesis from solid ammonium carbonate, at room temperature or elevated temperature, was studied.

Experimentals.

(I) Apparatus.

The apparatus used is shown in Fig. 1. A is a pressure-proof reaction vessel 10 mm in inner diameter, 7.5 mm in thickness and 45 mm in length. P are pistons 20 mm in length. To prevent leakage, at the tops of both pistons the self-tightening method of Bridgman's type, R, is used. The packing material is lead sheet 1~2 mm in thickness, but at over 200°C silver sheet is used in place of lead under pressure.

Pressure is produced by means of the intensifier which is already reported²⁾. The reaction vessel is put between the two pistons Q of the intensifier, and reaction system S is compressed hydrostatically by oil pump up to any desired pressure balanced with the pressure of the gas compressor. As the pressure of chamber C is determined directly by the pressure gauge G, the pressure of the reaction system can be calculated from the piston ratio of pistons P and Q ($P/Q = 1/9$). For example, when the pressure chamber is compressed to 30~1,200 kg/cm², the pressure of the reaction system elevated 270~10,800 kg/cm².

For the experiment at elevated temperature, an electric furnace H surroun-

1) M. Tokunaka, *J. Agr. Chem. Soc. Japan*, 10, 186 (1934)

2) R. Kiyama, *This Journal*, 19, 1 (1945)

ding the reaction vessel is used. Temperature is determined by a thermocouple in T of the reaction vessel.

(II) Materials.

(a) Ammonium carbonate.

Ammonium carbonate found in market is a mixture of $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and NH_4HCO_3 . The analytical result is:

$(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$	22.55%
NH_4HCO_3	76.52%
H_2O	0.93%

(b) Urea.

Commercial urea is recrystallized from aqueous solution and dried up in a desiccator with KOH.

(c) Additional materials.

In the experiment at room temperature, α -alumina, γ -alumina and NaCl are used as catalysts.

Alumina:

Alumina is made by heating aluminum nitrate. A part of this alumina is ignited to red heat for 15 hrs. (α -alumina). The other part of crude alumina is boiled and washed with water, and the precipitate is heated at $400 \sim 500^\circ\text{C}$ for 12 hrs. (γ -alumina). NO_3^- ions in both alumina are not detected by H_2SO_4 solution of diphenylamine.

NaCl:

NaCl guaranteed for analysis is used.

(III) Analytical method.

The amount of the conversion of ammonium carbonate to urea is analysed as follows: the total nitrogen is determined by the Kjeldahl method. On the other hand, the ammoniacal nitrogen is determined³⁾ by distillation at 40°C from an alcoholic alkali solution with aeration, without any danger of decomposing urea. The amount of the conversion to urea is determined from the difference of total and ammoniacal nitrogen. The experimental error of this method is

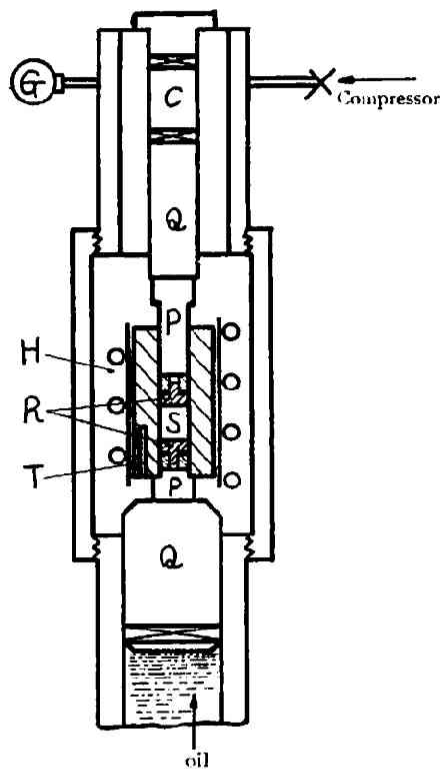


Fig. 1 Apparatus.

3) J. V. Yee and R. O. E. Davis, *Ind. Eng. Chem. (Anal. Ed.)*, 7 259 (1935)

within 0.2%. Another method of determination of urea is evacuation to constant weight at 60°C. Both methods agreed in the results perfectly. If necessary, the formation of urea is confirmed qualitatively by Xthanthydrol or Furfural.

Experimental results.

(I) Elevated temperature and high pressure.

The conversion of ammonium carbonate to urea under the hydrostatic pressure of 279~2,106 kg/cm², the temperature of 90~240°C, for 0.5~3.0 hrs. is shown in Table 1.

Table 1

Pressure (kg/cm ²)	Time (hrs.)	Conversion to urea (%)				
		90°C	150°C	180°C	210°C	240°C
2,106	0.5	—	4.69	13.23	16.52	16.84
2,106	1.0	—	—	15.13	16.30	16.65
2,106	3.0	—	—	—	16.33	—
1,071	0.5	0	5.62	14.10	17.30	17.48
558	0.5	—	5.36	12.10	16.23	16.37
279	0.5	—	5.11	8.48	13.62	13.84

Temperature is more effective than pressure on urea formation, but there is scarcely any temperature effect above 210°C. The pressure effect at a temperature over 240°C, under pressure of 1,000 kg/cm² gives the maximum yield. The time taken to reach equilibrium is within about 30 minutes at a temperature over 210°C under 2,106 kg/cm².

(II) Room temperature and high pressure.

Ammonium carbonate alone, ammonium carbonate with additional materials or urea are used in solid state as samples. At room temperature, the samples are compressed to pressure of 1,000~11,000 kg/cm² isothermally for 1 hour or adiabatically. In the case of necessity, this operation is repeated several times. The conversion of ammonium carbonate to urea or the decomposition of urea are determined by analysis. These results are shown in Table 2~8.

(a) Urea formation from ammonium carbonate.

(1) Pressure effect on ammonium carbonate alone is shown in Table 2. Under pressure of 1,000 kg/cm², urea is not formed from ammonium carbonate at room temperature and at 90°C, according to Table 1. When a pressure reached 4,770 kg/cm², about 2.4% of ammonium carbonate converts into urea at 30°C, but a

CHEMICAL REACTIONS UNDER ULTRA HIGH PRESSURE

35

pressure of 10,800 kg/cm² has less yield of urea. These results depend on the equilibrium of ammonium carbonate and urea, as shown in Table 6.

Table 2

Temp.: 25~30°C, No. of compression: one time.

Exp. No.	Pressure (kg/cm ²)	Compression method	Conversion to urea (%)
1	1,080	adiabatic	0
2	4,770	"	2.32
3 *	4,770	"	2.34
4	4,770	isothermal	2.48
5	10,800	adiabatic	1.04

* Pressure is applied individually to two samples equally divided, and analysis is done for the two together.

P. W. Bridgman reported^{4,5)}, observing the permanent chemical change by shearing stress under high pressure, that chemical alternation is limited to a surface layer between the iron vessel and the samples. Expecting the surface effect, therefore, Exp. No. 3 is performed (the surface area of the vessel being compared with others two times), but the result is negative. It means that the surface effect can not be recognized in these experiments.

(2) To confirm whether urea is formed or not from a saturated aqueous solution of ammonium carbonate as the same as from solid, an experiment is performed at room temperature and 4,770 kg/cm², but urea is not formed.

(3) Pressure effect on ammonium carbonate with additional materials (α -, γ -alumina and NaCl) are shown in Tables 3 and 4.

Table 3

Temp.: 25~30°C, No. of compression: one time,

Ammonium carbonate/Alumina: equi. weight.

Exp. No.	Pressure (km/cm ²)	Additional material	Compression method	Conversion to urea (%)
6	4,770	α -alumina	adiabatic	4.04
7	4,770	"	isothermal	3.99
8	10,800	"	adiabatic	2.74
9	4,770	γ -alumina	"	2.12
10	4,770	"	isothermal	2.12

4) P. W. Bridgman, *Proc. Am. Acad. Arts and Sci.*, **71**, 387 (1937)5) P. W. Bridgman, *Phys. Rev.*, **48**, 825 (1935)

Table 4
Temp.: 25–30°C

Exp. No.	Pressure (kg/cm ²)	Ammonium carbonate/NaCl (in weight)			Compression method	Conversion to urea (%)
		Step of compression				
		First	Second	Third		
11	4,770	1			adiabatic	3.60
12	"	1			isothermal	3.66
13	10,800	1			adiabatic	2.23
14	4,770	1/3			"	4.47
15	"	1	1	1	"	4.69
16	"	3/1	3/2	1	"	3.99
17	"	1	1/2	1/3	"	6.14

As the catalyst of urea synthesis the dehydrating effect of γ -alumina, which is effective^{6,7)} on urea synthesis from ammonia and carbon dioxide, can not be recognized. But hard and brittle substances, NaCl or so-called inactive dehydrating α -alumina, are effective on this reaction as a catalyst, especially the action of α -alumina is remarkable.

As for NaCl, increase of additional weight or step of compression give increasing yield of urea and a certain amount of NaCl added at a time is more effective than that added at three times.

As for the compression method, the difference between the effect of adiabatic compression and that of isothermal one is not shown. It is because of the large heat capacity of the reaction vessel or the speed of compression destined to the apparatus.

In the following experiments, the compression is adiabatic and the number

Table 5
Pressure: 4,770 kg/cm²

Exp. No.	Temperature (°C)	Additional material	Conversion to urea (%)
2	25	—	2.32
18	18	—	1.62
19	6	—	0.96
11	30	NaCl	3.60
20	16	"	3.05
21	6	"	1.78

6) M. Tokunaka, *J. Agr. Chem. Soc., Japan*, 11, 174 (1935)

7) C. Matignon and M. Frejacques, *Compt. Rend.*, 174, 455 (1922)

CHEMICAL REACTIONS UNDER ULTRA HIGH PRESSURE

37

of compression is one time.

(4) Seeing from the influence of room temperature on this reaction shown in Table 5, when temperature falls the conversion to urea decreases rapidly.

(5) Influence of duration of pressure applied is shown in Table 6.

Table 6

Sample: Ammonium carbonate alone, Temp.: 6°C, Pressure: 4,770 kg/cm².

Exp. No.	Duration (hrs.)	Conversion to urea (%)
22	3.0	1.00
23	1.5	0.96
19	immediately released	0.96

The experiments carried out in the duration of an instant, 1.5 hrs. or 3 hrs. give the same results. It affirms that the reaction finishes in a moment of pressure applied and the reaction process is based on the mechanical force.

(6) As a sample, a mixture of ammonium carbonate and urea is used. It is found that an equilibrium value of 5.26 % urea is obtained under 4,770 kg/cm² and 15°C as shown in Table 7.

It is expected that there is a chemical equilibrium among ammonium carbonate, urea, carbon dioxide and water.

Table 7

Temp.: 15°C

Exp. No.	Pressure (kg/cm ²)	Urea (%)	
		Before pressure applied	After pressure applied
24	4,770	21.60	11.52
25	"	12.96	6.10
26	"	5.26	5.26
27	10,800	21.10	14.08

(7) According to increasing pressure vapor tension of ammonium carbonate decreases exceedingly. When a pressure of nearly 5,000 kg/cm² is applied, ammonia odour of the salt swept away and the mechanical strength of the compressing sample is sufficient for transportation.

The stability of the pressure applied sample is determined by measuring the decrease of weight in the air or in vacuum desiccator with conc. H₂SO₄. These results are shown in Figs. 2 and 3.

Although the difference between the stability of the samples of 1,000 kg/cm² compressed and that of the original sample is not recognized, the stability of 4,770 kg/cm² pressure applied is 10 times or more in the atmosphere as that of the original sample and larger than that of 10,000 kg/cm² pressure applied. This result is in accord with that

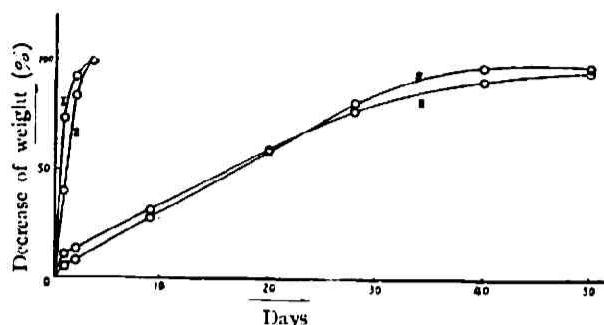


Fig. 2 Stability of pressure applied samples, ammonium carbonate alone, in the atmosphere at 30~35°C.
I: original (pressure not applied), II: 1,000 kg/cm², III: 4,770 kg/cm², IV: 10,800 kg/cm².

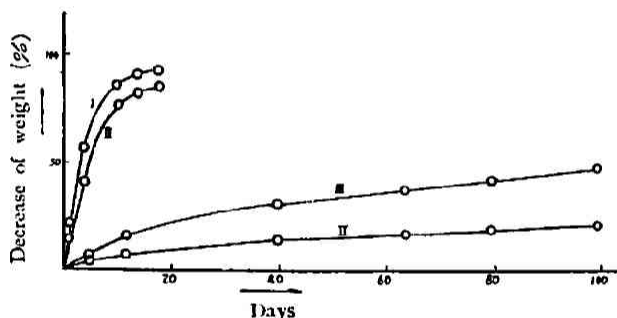


Fig. 3 Stability of pressure applied samples, mixture of ammonium carbonate and NaCl (in equi. weight).
I: 10,800 kg/cm², II: 4,770 kg/cm² in the atmosphere at 60° C. III: 10,800 kg/cm², IV: 4,770 kg/cm² in the desiccator with conc. H₂SO₄ at 0~8°C.

the conversion to urea at 4,770 kg/cm² is larger than at 10,800 kg/cm². It is observed that the pressure applied sample of a mixture of ammonium carbonate and NaCl is more stable than that of ammonium carbonate alone, and 4,770 kg/cm² pressure applied sample of a mixture is so stable that the decrease of weight shows only 21 % for 100 days at room temperature in a

vacuum desiccator with conc. H₂SO₄.

(b) Pressure effect to urea.

P. W. Bridgman reported^{8,9)} that in polymorphic transition of pure urea the transition line of urea (I) and urea (II) lies between 4,300 atm., 0°C and 6,750 atm., 102.3°C, and urea does not decompose even in duration of 1 hr. at 150~200°C under a pressure of 30,000 kg/cm². It is also reported that the decomposition of urea occurs at 130°C under the atmospheric pressure, but it is supposed at high pressure.

The decomposition of urea, however, is observed in the experiment of

8) P. W. Bridgman, *Proc. Am. Acad. Arts and Sci.*, **52**, 106 (1916)

9) P. W. Bridgman, *ibid.*, **72**, 227 (1938)

CHEMICAL REACTIONS UNDER ULTRA HIGH PRESSURE

39

equilibrium of ammonium carbonate and urea. Therefore, it is examined whether urea is decomposed or not near the transition conditions by adiabatic compression of urea alone, urea with water or with NaCl which is effective to urea formations. But, these examinations are negative to detected NH_4 ion by Nessler's solution in all cases as shown in Table 8.

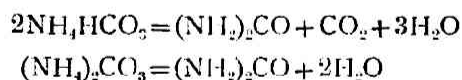
Table 8
Temp.: 25°C

Exp. No.	Pressure (kg/cm ²)	Sample (ratio in weight)	Pressure applied duration	Nessler reagent
28	4,950	Urea	Immediately released.	—
29	"	Urea + H_2O (10 : 1)		—
30	10,800	Urea + NaCl (1 : 1)		—
31	"	Urea + NaCl + H_2O (5 : 5 : 1)		—
32	"	Urea + H_2O (10 : 1)		—
33	4,950	Urea + H_2O (10 : 1)	3 hrs.	—

Considerations.

The experiments at room temperature and high pressure give some significant results. For urea synthesis, the rise of temperature is an indispensable condition, but in these experiments urea is synthesized instantly at room temperature by mere compression of solid ammonium carbonate to higher pressure known in the course of urea synthesis from carbon dioxide and ammonia.

This reaction process will be considered as follows. In the course of this synthesis the water separated from the reaction system is observed. It is clear that conversion of ammonium carbonate to urea occurs by such dehydrating action as :



As an intermediate of this reaction, the existence of ammonium carbamate $\text{NH}_4\text{CO}_2\text{NH}_2$ is expected, but it is not observed by detection of CO_2NH_2 ion¹⁰. Also it is imagined that ammonium cyanate NH_4CNO may be produced by dehydration of ammonium carbonate as the same way as urea is formed. To confirm the existence of cyanate, after the unchanged ammonium carbonate of a pressure applied sample is isolated with calcium nitrate, the detection of CNO ion¹¹ with

10) R. Kuki, *J. Soc. Chem. Ind., Japan*, **43**, 180 (1940)

11) J. Walker and F. J. Hambly, *J. Chem. Soc.*, **67**, 746 (1895)

silver nitrate is tried out, but it is negative. It seems that, even if ammonium cyanate is formed, it may be converted to more stable urea by molecular rearrangement. It will be clear that the Solvay Process in dehydrated water from urea formation occurs as a side reaction in the case with NaCl as catalyst.

Now, the origin of this new chemical reaction may be considered as follows. In the compression method of this experiment, the pressure is approximately hydrostatic and mainly transmitted from crystal grain to grain as a mechanical force since the solid sample itself is directly compressed by piston without the pressure transmitting fluid, as R. B. Jacob already pointed out¹²⁾. It is expected, therefore, the shearing stress presents inevitably. It is considered that shearing stress acts on atom and molecule as a result of mechanical force to all grains and produces not only chemical alternation of the surface layer of iron vessel and samples, but that of the whole system in the reaction vessel. That is to say, the mechanical force leads molecules to rearrangement of atoms and tears out, and at the same time dehydration that is conversion of ammonium carbonate to urea, occurs. If the shearing stress is not present, urea is not formed at room temperature as known in the experiment of saturated aqueous solution of ammonium carbonate. Considering the action of catalyst, it is crushed to fine powder and is effective as mechanical force acts on the reactant crystals. The action of the catalyst of this sort is perfectly mechanical and is not known until now. From the above consideration, it may be expected that the origin of this chemical reaction is based on a mechanical force.

This consideration is moreover supported by the experimental results that urea is formed in a moment of pressure applied and increase of compression number give the increasing yield of urea.

The result of the pressure effect on the urea and water system is inconsistent with the experiment of equilibrium. It seems that an inhibitor in the course of the decomposition of urea exists and it can not be destroyed by such shearing stress applied in the existence of water.

It is clear that increase of the stability of pressure applied samples is based on the urea formation and partially the diminution of surface by compression.

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12) R. B. Jacob, *Phys. Rev.*, **54**, 468 (1938)